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Ultrasonic dispersion and relaxation in morpholine

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Ultrasonic methods for the investigation of the physical properties of matter form an important branch of physical research. Many laboratories have apparatus to measure the velocity with a fair accuracy. However, measurement of ultrasonic absorption is not that easy. This paper discusses a method, to find the compressional relaxation time (τ) in morpholine, using the property of bulk viscosity of the liquid, in terms of velocity alone. Earlier data on this liquid which were obtained in this laboratory (Seshadri *et al* 1984) are used to make these calculations. In addition, some values are obtained by extrapolation. An understanding of the various intermolecular forces in the liquid can be achieved with a knowledge of τ and its variation with temperature (T).

The bulk viscosity coefficient (η_v^*) of a liquid becomes (Narasimham 1969) complex (*) and frequency (ω)-dependent parameter under the action of an ultrasonic wave, and can be expressed as :

$$\eta^* = \eta_1 - i\eta_2 = \eta_v^* - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)]/(1 + i\omega\tau) \tag{1}$$

$\eta_1(\omega)$ and $\eta_2(\omega)$ are the real and imaginary parts of η_v^*. They are responsible for absorption and dispersion of the wave, respectively. The real and imaginary parts can be written as :

$$\eta_1(\omega) - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)]/(1 + \omega^2\tau^2) \tag{1a}$$

$$\eta_2(\omega) = [\eta_1(0) - \eta_1(\infty)][\omega\tau/(1 + \omega^2\tau^2)] \tag{1b}$$

The Navier-Stokes (Tisza 1942) equations for η_1 and η_s can be expressed as,

$$\eta_1 + (4/3)\eta_s = 2\rho_0 V_\omega^3(\alpha/\omega^2) \tag{2a}$$

$$\omega\eta_2(\omega) = 2\rho_0 V_0(V_\omega - V_0) \tag{2b}$$

From the above equations, we can see that

$$[\omega\eta_2(\omega)]_\infty = [(\eta_1(0) - \eta_1(\infty))/\tau][\omega^2\tau^2/(1 + \omega^2\tau^2)]_\infty$$
$$= [\eta_1(0) - \eta_1(\infty)]/\tau \tag{3a}$$

since,

$$(1+\omega^2\tau^2) \to \omega^2\tau^2, \text{ as } \omega \to \infty. \tag{3b}$$

where ($\omega \to \infty$) refers to a reasonably high ultrasonic frequency and ($\omega \to 0$) refers to very low frequencies, ρ_0 is the density of the liquid in the absence of the wave, η_s is the shear viscosity coefficient and α is amplitude-absorption coefficient of the wave. We can also see from the above equations that

$$[\eta_1(0)-\eta_1(\infty)]/\tau = [\omega\eta_2(\omega)]_\infty = 2\rho_0 V_0(V_\infty - V_0) \tag{4}$$

$$[\eta_1(0)-\eta_1(\infty))/\tau][\omega^2\tau^2/(1+\omega^2\tau^2)] = 2\rho_0 V_0(V_\omega - V_0) \tag{5}$$

Dividing eq. (4) by eq. (5), we get

$$(\omega^2\tau^2+1)/\omega^2\tau^2 = (V_\infty - V_0)/(V_\omega - V_0) \tag{6}$$

and

$$\tau = (1/\omega)[V_\omega - V_0)/(V_\infty - V_\omega)]^{1/2} \tag{7}$$

It may be noted that eq. (7) for τ depends only on dispersion. This is obtained by combining eqs. (1b) and (2b). τ can be obtained by combining eqs. (1a) and (2a) also. But this would be more complicated. Evaluation of τ according to eq. (7) requires V_0, V_ω, ω and V_∞. Data taken in our laboratory, for morpholine, for variation of V with ω are utilised for this purpose. However, these data (Seshadri *et al* 1984) do not contain all required values. Hence, these data are extrapolated to very low ($\omega \to 0$) and very high ($\omega \to \infty$) frequencies, to obtain V_0 and V_∞. The extrapolation is done keeping in view the general variation of V with ω, as indicated in Figure 1. V increases with ω and decreases with tempera-

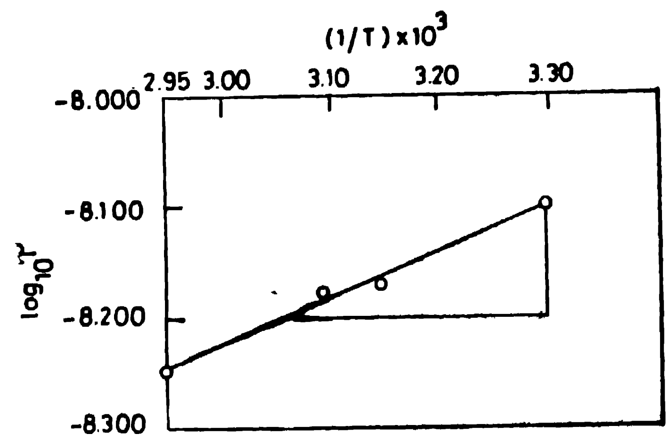

Figure 1. Variation of V_ω with ω.

ture (T). Further, $\omega = 2\pi f$ and V_ω is chosen at $f \simeq 10$ MHz. Since morpholine is a liquid of low shear viscosity, variation of V with ω and T is expected to be low. Hence V_∞ may be around 1600 to 1700 m/sec in the temperature range 20°C to 80°C. It is expected that 10 MHz may be in the relaxation region. The extrapolated values, obtained with these considerations, are given in Table 1, at different four temperatures. The values of $(1/T)\times 10^{3}$ and $\log_{10}\tau$ corresponding to the various values of temperature (T) are : 3.300, 3.145, 3.096, 3.003 and −8.0969, −8.1740, −8.1798, −8.2457, respectively. It may be seen that there is a general

Table 1. Extrapolated values of acoustic parameters for morpholine.

S. No.	Temp Å	V_0 m/s	V_ω m/sec	$f=\omega/2\pi$ s^{-1}	V_∞ m/sec	$\tau\times 10^{9}$ sec using eq. (7)
1.	303	1453	1494	10 MHz	1658	8.00
2	318	1397	1443	10 MHz	1636	6.70
3.	323	1375	1413	10 MHz	1633	6.61
4.	333	1339	1372	10 MHz	1631	5.68

decrease of V with T, as expected. However, the variation in V_∞ is quite small, especially, after about 45°C. It may be added that (dV_∞/dT) is generally less than (dV_ω/dT) for low or medium values of ω. τ decreases with T as expected. τ can be fitted into the equation

$$\tau=\tau_0 \exp (W/kT) \tag{8}$$

where τ_0 is a constant, independent of T and W is the activation energy for the liquid. W is a measure of the intermolecular binding in the liquid. The magnitude of τ seems to be reasonable. Figure 2 gives a plot of $\log_{10}\tau$ vs $(1/T)$. The slope

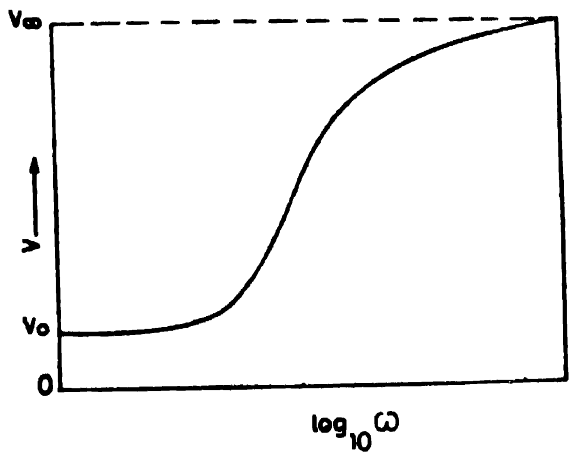

Figure 2. Variation of $\log_{10}\tau$ with $(1/T)$.

of this graph $= d(\log_{10}\tau)/d(1/T) = (W/2.303k)$, where k is the Boltzman's constant $=(0.1/(0.24\times 10^{-3})=1000/2.4$. Hence $W=0.083$ eV. This seems to be a fairly good value for W, for liquids with relatively low association

In conclusion, it may be added that the concept of bulk viscosity of a liquid makes it possible to calculate many ultrasonic and molecular parameters of a liquid, when fairly accurate ultrasonic data are available.

References

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